

ANODIC OXIDATION OF CYCLIC HYDROCARBONS

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In order to obtain efficient practical direct hydrocarbon fuel cells for military use, it is necessary to oxidize the components of logistically available fuels. Military specifications¹ allow these fuels to contain as high as 25% aromatics and 5% olefins. Recently Luksha² found that a Niedrach-Alford Teflon bonded platinum electrode with phosphoric acid electrolyte at 150°C could tolerate a fuel containing up to 5% olefins, 1% aromatics, 5% six ringed naphthenes, 15% five ringed naphthenes and the remainder saturated normal or isooctane with an increase loss of only 50 mv in polarization from that of pure octane. Previously we had reported³ the adsorption characteristics of some of these representative compounds on bright platinum wire in 85% H_3PO_4 at 130°C. For all of the compounds studied, the rate of adsorption appeared to be diffusion controlled. Benzene adsorbed the most rapidly; cyclohexene and cyclopentene adsorbed the next fastest and both at the same rate; hexene-1 and hexene-2 also adsorbed at the same rate, but less rapidly than the unsaturated cyclic compounds; and cyclohexane and cyclopentane had the lowest rate of diffusion. For all compounds, maximum adsorption was between 0.2 and 0.4V. The highest steady state coverage for a specific concentration was obtained for the most rapidly adsorbing species. The maximum amount of adsorption at each potential follows the same order as did the rate of adsorption (i.e. benzene adsorbed the most).

In fuel cell tests,² it has been found that cyclohexyl compounds affect octane performance more adversely than five c-ringed naphthenes and they do not behave like normal saturated hydrocarbons. Open circuit values indicated dehydrogenation to benzene was occurring for the six member ringed compounds; however, in the initial adsorption studies on a wire electrode, cyclohexane appeared to behave as a normal saturated hydrocarbon. To obtain more evidence as to whether there was dehydrogenation under our conditions, the composition of electrochemically adsorbed species formed from benzene and cyclohexane was investigated using cathodic and anodic desorption techniques developed by Brummer.

Experimental

The experimental set up was similar to that which we have described previously.⁵ In brief, the electrochemical studies were performed on a flamed bright platinum wire of thermocouple grade platinum of geometric area 0.5 cm² maintained at 130°C in 85% H_3PO_4 . The acid had been pretreated with hydrogen peroxide and was contained in a standard three compartment electrochemical cell made of quartz. The reference electrode was the dynamic hydrogen reference electrode described by Giner.⁶ The hydrocarbon was introduced into the working compartment by using an argon carrier gas through a glass tube containing organic compound maintained at a controlled temperature to give the desired partial pressure. For low partial pressures, the organic was contained in a tube cooled in an ice-methanol bath. For higher partial pressures, the tube containing the hydrocarbon was heated in an oil bath to the desired temperature. Phillips research grade hydrocarbons of 99.6 mole % purity were used in all cases.

In order to obtain a reproducible platinum surface for the electrochemical measurements, potentiostatic procedures similar to those of Brummer⁷ and Gilman⁸ were employed. Essentially, the electrode was held at 1.35 V for 1 min., the last 30 sec without stirring, at 0.05V for 10 msec, and then maintained at a potential of interest for varying times before examining the surface state of the electrode with an anodic or cathodic galvanostatic pulse.⁷ Potential sequences were obtained by switching of a series sequence of potentiometers with H₂-wetted relays. Time intervals at the potentials were controlled by Tektronix Type 162 waveform generators.⁹ The potentials were applied to the cell through the input of a Wenking potentiostat.

All areas are based on real electrochemical areas with 210 μcoul equal to 1 cm^2 of real area as obtained from deposition of a monolayer of hydrogen with a cathodic galvanostatic charging curve.¹⁰

Results and Discussion

Anodic galvanostatic charging (Q) using current densities from 500 μamp to 150 ma/cm^2 gives a reliable estimate of oxidizable material on an electrode.⁷ The charge occurring from the oxidation of the electrode and adsorption of H_3PO_4 under argon is subtracted from the charge obtained with organic reactant. To obtain the amount of irreversibly adsorbed material on the electrode, cathodic galvanostatic pulses are used. The ratio of hydrogen deposition obtained in the presence of organic with that obtained in an argon atmosphere gives θ_{H} . The fraction of the surface covered by organic material is $1 - \theta_{\text{H}}$. The initial adsorption studies with benzene³ indicated that at higher concentrations (200 mm partial pressure) of benzene, 15% of the electrode was covered with material after adsorption at potential for 1 msec, the least amount of time of adsorption that could be reproducibly measured. In order to have a clean surface at initial adsorption, benzene at a partial pressure of 5 mm was used in these studies. Since cyclohexane³ adsorbed very slowly at the lower concentrations and at higher partial pressures behaved like normal saturated hydrocarbons,^{5,7,11} a higher concentration was used. This would also enable dehydrogenation to benzene to be detected more easily.

Maximum Amount of Adsorption

The adsorption of benzene and cyclohexane appears to be initially diffusion controlled, the rate of adsorption then decreases and the surface concentration of adsorbed species reaches a constant maximum value.³ This value is reached within 30-60 seconds at all potentials except with the low concentration of cyclohexane where steady state coverage is not obtained until 300 seconds. Figure 1 shows the maximum amount of adsorption obtained from anodic galvanostatic pulses as a function of potential for benzene at 5 mm pressure and cyclohexane at 200 mm pressure. The electrode is pretreated as mentioned, held at the potential of interest for 2 minutes and then treated with an anodic galvanostatic pulse of 50 ma/cm^2 . Both compounds have appreciable adsorption from 0.05 to 0.80 V, and benzene even has adsorption at 0.9 V. Between 0.2 and 0.4, maximum adsorption is observed. There is not, however, a sharp maximum at 0.2 V as has been observed with n-paraffins,^{7,11} but more of a bell shaped appearance for both of the compounds. Figure 2 is a plot of the maximum fraction of the surface covered vs potential as obtained after 2 minute adsorption with a cathodic galvanostatic pulse of 50 ma/cm^2 . These measurements indicate maximum coverage for both compounds at 0.2 and 0.3 V. Both figures (1) and (2) indicate that the maximum amount of surface coverage does not differ too much for both compounds though it must be kept in mind that there is a much lower concentration

of benzene. Figure 2 also shows maximum amount of coverage for 200 mm pressure of benzene. Maximum amount of adsorbed species for a specific compound might be expected to be independent of concentration if long enough times of adsorption at potential are maintained, and little or no oxidation is taking place. Figure 2 indicates about 68% maximum coverage with benzene and 65% coverage with cyclohexane - numbers within experimental error of each other. Compounds of similar size and reactivity would be expected to occupy same space of the electrode. The maximum charge to oxidize the adsorbate is slightly higher for the cyclic hydrocarbons than the n-paraffins.^{4,7,11,12}

These results compare with 50% electrode coverage in the region 0.3-0.5V vs normal hydrogen electrode obtained by Bockris et al.¹³ using radiotracer techniques for benzene adsorption in H_3PO_4 at 50°C.

Type of Adsorbed Species

Gilman,¹⁴ Niedrach¹⁵ and Brummer^{4,11,12} have obtained evidence for several types of intermediates adsorbed on the electrode surface with normal saturated hydrocarbons or ethylene as reactant. Part of the adsorbate designated $\text{CH-}\gamma$ can be cathodically desorbed and is thought to contain only C and H. Another CH material not removed by cathodic treatment and seems to be a combination of a CH polymer ($\text{CH-}\beta$) and a more highly oxidized material thought to contain at least one C-O bond (O-type). To determine whether benzene and cyclohexane give the same type of adsorbed intermediates - specifically whether cyclohexane dehydrogenates to benzene - the composition of the steady state adsorbed residues was investigated. Cathodic and anodic desorption techniques similar to those used by Brummer⁴ have been employed. After the usual pretreatment, the electrode was held at a potential for 60 sec at which point steady state coverage was obtained. Then the potential was lowered to 0.01 V where little or no adsorption occurred (benzene had appreciable adsorption at potentials higher than 0.01 V, but not at 0.01 V). At 0.01 V part of the adsorbate, $\text{CH-}\gamma$, desorbs. The potential was held at 0.01 V for various periods of time after which the surface was examined with a galvanostatic pulse. $Q_{\text{CH-}\beta \text{ \& C-O}}^{\text{res}}$, the charge required to oxidize the remaining adsorbed species to CO_2 , and θ_{org} , the fraction of the surface occupied by the remaining organic species C-O and $\text{CH-}\beta$ obtained from the cathodic stripping curve were followed as a function of time. Before applying the galvanostatic pulse, the potential was raised to oxidize any H_2 adsorbed at 0.01 V. In the time necessary to oxidize H_2 off, there is no readsorption of organic material. The slope of Q vs θ plot gives $[e]$ the number of electrons released per covered site during oxidation of adsorbate. Changes in $[e]$ during the desorption of a given adsorbed species are taken as evidence for the presence of different adsorbed species.⁴ Figure 3 is an example of Q vs θ plot for benzene and cyclohexane for which steady-state was obtained after adsorption for 60 sec. at 0.4 V. Desorption proceeds from the right to the left of the figure. The easiest material to be desorbed occurs at the right. For both compounds, a constant value of Q and θ are obtained after desorbing at 0.01 V for 5 seconds which indicates all of the $\text{CH-}\gamma$ is desorbed. Both compounds give a slope corresponding to 5.5 electrons per covered site on the path to oxidation. A methylene group (CH_2) in cyclohexane would require 6 electrons to oxidize completely to CO_2 , a methine group (CH) of benzene requires 5 electrons to oxidize completely to CO_2 . This result indicates that the cathodically desorbable material might be an equilibrium mixture of benzene and cyclohexane. There is a certain amount of scatter in the plotted points; therefore, it is difficult to distinguish whether there are two separate slopes: one equal to 5 electrons and another equal to 6. Thermodynamic equilibrium data for the gas phase dehydrogenation reaction:



indicates that there would be an equimolar amount of the two compounds.¹⁶ There is substantial evidence that the $\text{CH}-\Psi$ material is a composite of several species. Using a fuel cell electrode and propane as the reactant, Grubb¹⁷ and Barger and Savitz¹⁸ found that upon cathodic desorption, methane and ethane were observed with the gas chromatograph. Brummer has not examined the fine structure of $\text{CH}-\Psi$ for propane or hexane adsorption on a wire electrode. Using our experimental set-up, inconclusive results were obtained for the $\text{CH}-\Psi$ from propane adsorption, as the species occupied only 6% of the covered surface and $\text{CH}-\Psi$ had desorbed completely at 0.01 V in 100 msec. Figure 3 also indicates a small part of the surface covered with a highly reduced species for the benzene adsorbed species. This could be a polymeric material although in desorption experiments with propane at a fuel cell electrode, no species higher than propane was observed in the gas chromatograph.¹⁸ Figure 4 indicates that the 5.5 electron species appears to be relatively potential independent from 0.1 to 0.7 V. At 0.05 where there is most likely to be hydrogen along around with hydrocarbon, a lower number of electrons is obtained. The oxidation of hydrogen would account for 1 [e] and the average of the mixture would be lower. These results do not tell us whether the relative amount of the species which comprise $\text{CH}-\Psi$ is potential independent. Barger found the ratio of methane to ethane formed on cathodic desorption was very potential dependent.¹⁸ Definite proof of whether there is an equilibrium of cyclohexane and benzene and the relative amounts is currently being obtained with gas chromatographic procedures.¹⁸ The value of 5.5 electrons is obtained for species which have been adsorbed at the potential of interest for 120 sec to indicate steady state of adsorption had been obtained at 60 sec.

The total amount of $Q_{\text{CH}-\Psi}$ is defined as $Q_{\text{ads}}^{\text{org}} - Q_{\text{res}}^{\text{org}}$ after desorption for 5 sec at 0.01 V. The charge of $\text{CH}-\Psi$ for benzene and cyclohexane with potential varies similarly to that of the total charge for each compound with a maximum amount between 0.2 and 0.4 V (figure 5). This is similar to the results for propane⁴ and n-hexane¹¹ except there is more $\text{CH}-\Psi$ for benzene and cyclohexane. At 0.2 V, 650 $\mu\text{coul}/\text{rcm}^2$ charge to oxidize $\text{CH}-\Psi$ is observed for benzene, 600 $\mu\text{coul}/\text{rcm}^2$ for cyclohexane, 400 $\mu\text{coul}/\text{rcm}^2$ for n-hexane,¹¹ and 175 $\mu\text{coul}/\text{rcm}^2$ for propane.⁴ In both cyclohexane and benzene from 0.1 V to 0.4 V, 70% ($\pm 5\%$) of the covered surface is with $\text{CH}-\Psi$. At 0.5 to 0.7 V, about 60% of the covered surface is with $\text{CH}-\Psi$. As oxidation increases, less of the surface should be covered by the more reduced species.

In order to determine the composition of the remaining adsorbed species, desorption at more anodic potentials was pursued. The electrode is pretreated, held at a given potential for 60 sec at which point steady state coverage has been obtained, and maintained at 0.01 V for 10 seconds to desorb all of the $\text{CH}-\Psi$ material, returned to 0.4 V to oxidize H_2 formed at 0.01 V, and then raised to a potential of 1.0 V where it is held for varying amounts of time before examining the surface with galvanostatic charging curves. The potential is lowered to 0.40 V before making the measurement to reduce any oxide formed. No readorption of organic material occurs during the time at 0.4 V. The slope of a $E_{\text{vs}}Q$ plot gives a value of 1.95 electrons per site when it is oxidized to CO_2 (figure 6). This species is potential independent from 0.1 to 0.8 V as shown in figure 4. There is a certain scatter at 0.3 where a value of 1.4 electrons is obtained. It is unexpected that both cyclohexane and benzene should give the same deviation. Since we are dealing with a relatively small charge oc-

cupying only 15% of the total electrode coverage (up to 30% of the adsorbed species), there is more likely to be some uncertainty than where there is more of the O-type and one must be cautious in comparing with other O-type species. Brummer has found O-type species for propane for which $[e]$ is 1.3⁴ and covers about 80% of the electrode at 0.4 V and for n-hexane for which $[e]$ is 1.4¹¹ and covers 40% of the electrode. Our value for the cyclic compounds is higher, but repeating Brummer's experiments with propane we obtain $[e]$ of 1.1 and covers 70% of the electrode. With benzene and cyclohexane, we have been unable to desorb all of the material on the electrode at 1.0 V, even after setting for 120 sec. About 5% of the surface remains covered with a species requiring a charge of 50 $\mu\text{coul}/\text{cm}^2$ to oxidize it.

These results do not give the answer as to what the sequence of steps from benzene or cyclohexane to CO_2 are. On a fuel cell electrode, both cyclohexane and benzene were found to be 1/4 as reactive as hexane and 1/8 as reactive as propane.¹⁹ Benzene is slightly less reactive than cyclohexane. The decrease in reactivity might be explained by the fact there is much more $\text{CH-}\nabla$ for cyclohexane and benzene than propane and its oxidation is the slow step for the overall oxidation. Whether this $\text{CH-}\nabla$ is unreacted benzene or cyclohexane, a mixture of it and some of the possible cracking products (C_1 , C_2 , C_3 etc) is being determined by adsorbing on a fuel cell electrode, desorbing cathodically, and analyzing the desorption products with a gas chromatograph.

ACKNOWLEDGEMENT

The interest and helpful suggestions of Dr. H.J. Barger, Jr. is gratefully acknowledged.

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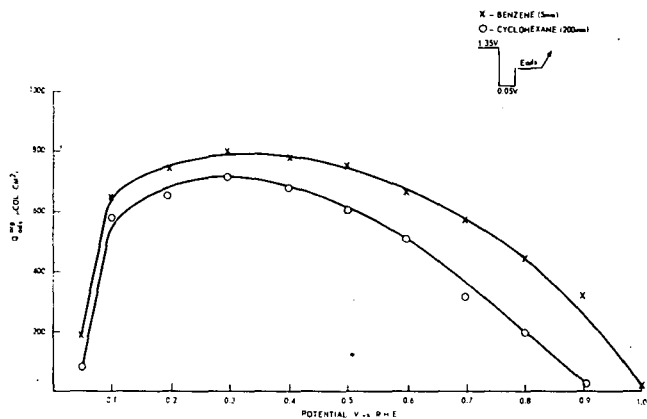


Figure 1. Steady-state adsorption of benzene and cyclohexane as a function of potential

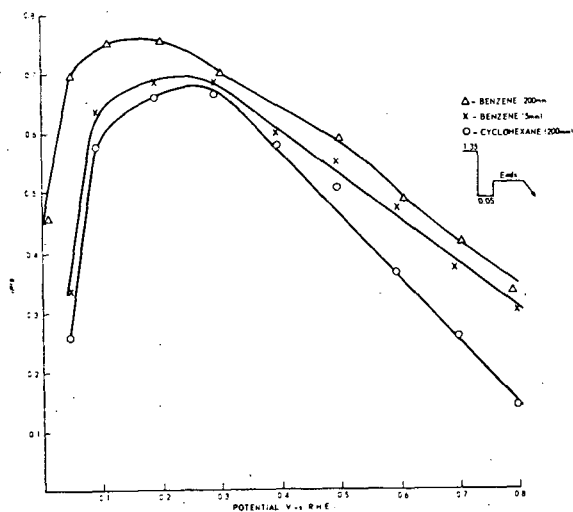


Figure 2. Maximum fraction of surface of electrode covered for steady-state adsorption of benzene and cyclohexane as a function of potential.

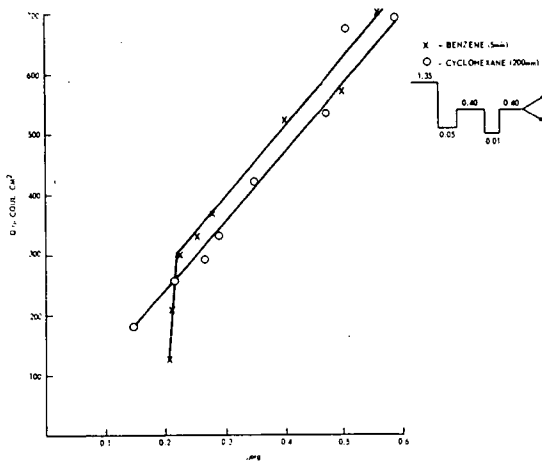


Figure 3. Desorption at 0.01 V of cathodically desorbable material adsorbed at 0.40 V.

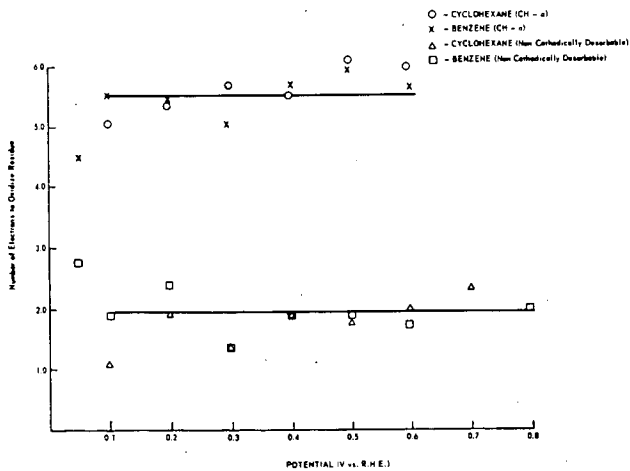


Figure 4. Electrons per covered site to oxidize residue to CO_2 as a function of potential.

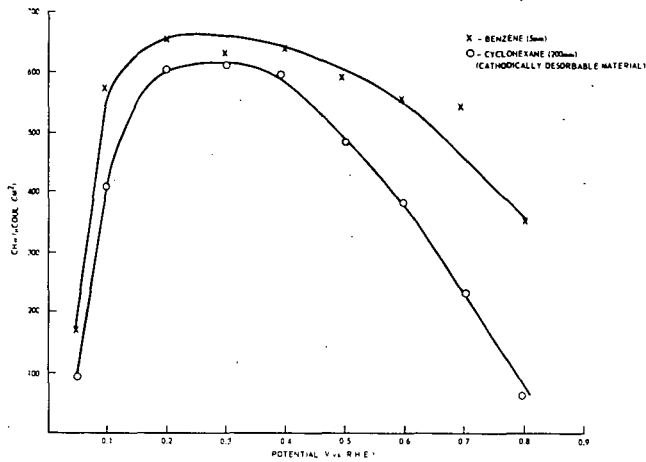


Figure 5. Charge lost on cathodic desorption ($\text{CH}-4$) for benzene and cyclohexane as a function of potential.

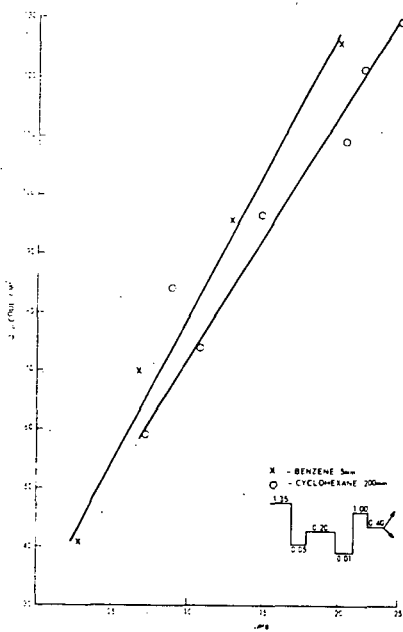


Figure 6. Desorption at 1.0 V after prior cathodic desorption.